

3,5-Dimethyl-2*H*-pyrazol-1-ium diphenylphosphate

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## Key indicators

Single-crystal X-ray study

*T* = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

*R* factor = 0.048

*wR* factor = 0.130

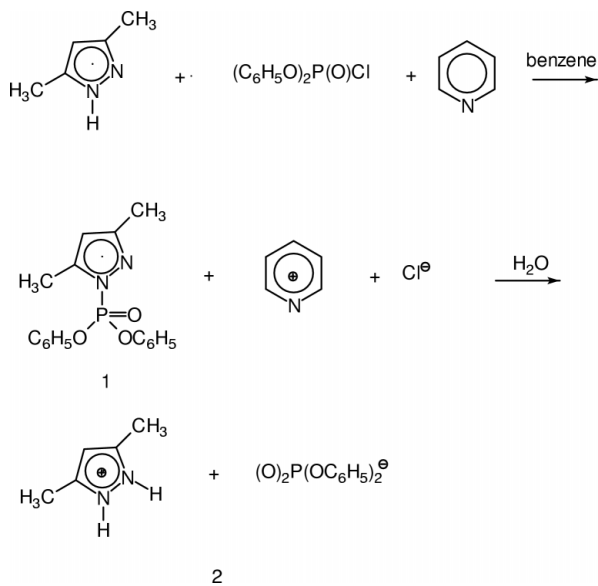
Data-to-parameter ratio = 14.5

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title complex,  $\text{C}_5\text{H}_9\text{N}_2^+ \cdot \text{C}_{12}\text{H}_{10}\text{O}_4\text{P}^-$ , is reported. The  $\text{C}_5\text{N}_2\text{H}_9^+$  cation and  $\text{PO}_2(\text{OC}_6\text{H}_5)_2^-$  anion are linked by  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds and form chains along the *b* axis. The geometry around the P atom indicates a distorted tetrahedron.

## Comment

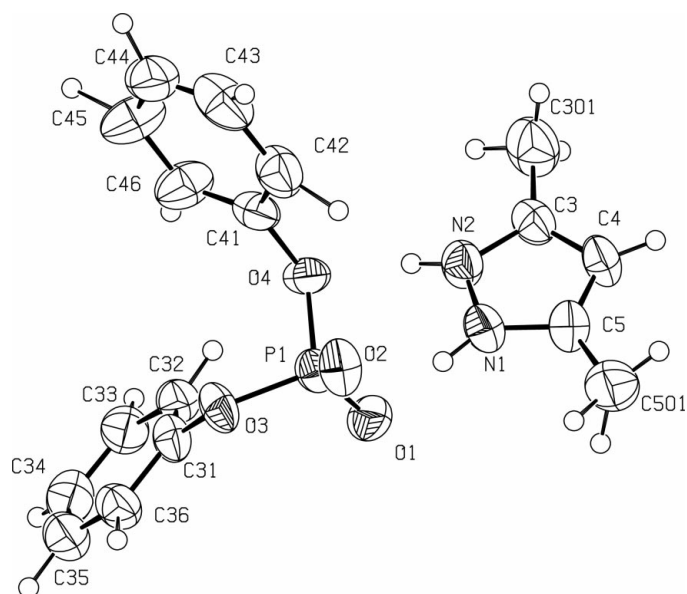
Anticancer chemotherapy is a very important issue in both medicinal chemistry and pharmacology (Lippert, 1999). The aim of this work was the synthesis and investigation of the chemical properties and biological activity of the novel phosphonate esters of diazole: the development of the synthetic methods for these compounds, determination of their structures by means of spectroscopic as well as X-ray methods, and the evaluation of their bio-active properties (Okada *et al.*, 2001; Rinke *et al.*, 2001; Boduszek, 1996). Knowledge of the structure will help in the design and synthesis of new ligands for Pt complexes.



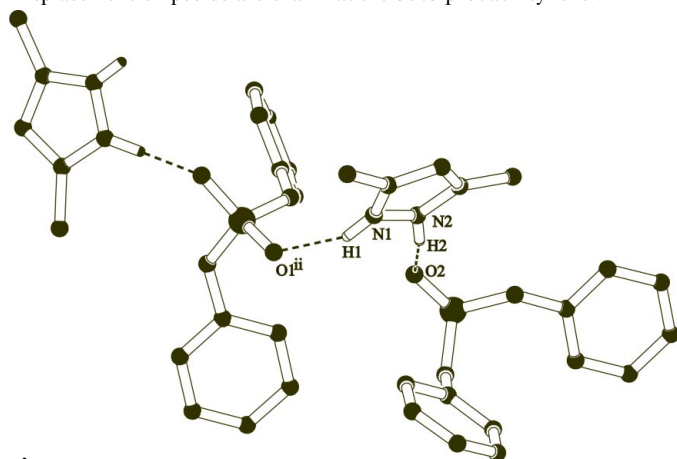
X-ray studies confirm that the title compound, (2), exists in the crystal state in the ionic form. The  $\text{C}_5\text{N}_2\text{H}_9^+$  cation and  $\text{PO}_2(\text{OC}_6\text{H}_5)_2^-$  anion are linked by  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds (Table 2, Fig. 2). The combination of two hydrogen bonds provides a second level motif of type  $C_2^2(7)$  (Bernstein *et al.*, 1995). Finally, the molecules form chains along the *b* axis (Fig. 3).

Moreover, aromatic  $\pi-\pi$  stacking interactions between pyrazole rings were found, which further stabilize the molecular arrangement of the structure. The distance between the centroids of the pyrazole rings  $Cg \cdots Cg^i$  [symmetry code: (i)

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**Figure 1**  
The ORTEP drawing of title compound, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
Hydrogen bonds between molecules [symmetry code: (ii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ]. All H-atoms except H1 and H2 are omitted for clarity.

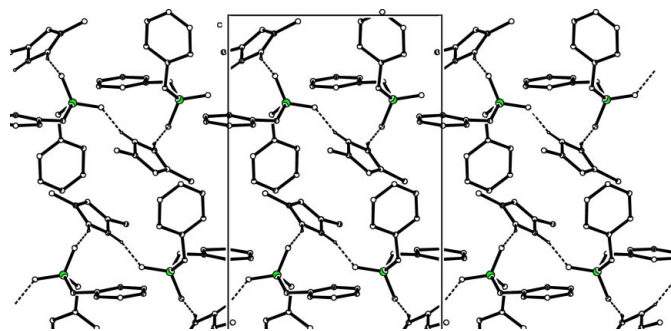
$-x, 1 - y, 1 - z$ ] is 4.21 (1) Å. The perpendicular distance between the rings is 3.64 (1) Å.

The bonds and angles around the P atom indicate a slight distortion of the tetrahedron, with the angles ranging from 104.24 (9) to 120.31 (11)° (see Table 1). The two bond distances P1–O1 and P1–O2 are almost equal in length [1.471 (2) and 1.477 (2) Å, respectively], thus confirming delocalization of these bonds in the solid state.

The benzene and pyrazole rings are planar within experimental error. The dihedral angle between the benzene rings is 83.2 (1)°. Bond distances and angles are in good agreement with expected values (Allen *et al.*, 1987).

## Experimental

Spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , NMR, IR) and elemental analysis showed that the diphenyl-3,5-dimethyl-1-pyrazolylphospho-



**Figure 3**  
The chains of molecules along the *b* axis of the unit cell, linked by hydrogen bonds. All H-atoms except H1 and H2 are omitted for clarity.

nate (1) is formed in the reaction of 3,5-dimethyl pyrazole with diphenyl chlorophosphate in the presence of anhydrous pyridine. In the presence of water, compound (1) is rapidly converted into compound (2).

## Crystal data

$\text{C}_5\text{H}_9\text{N}_2^+ \cdot \text{C}_{12}\text{H}_{10}\text{O}_2\text{P}^-$   
 $M_r = 346.31$   
Monoclinic,  $P2_1/n$   
 $a = 8.890$  (1) Å  
 $b = 10.970$  (2) Å  
 $c = 17.714$  (1) Å  
 $\beta = 90.41$  (1)°  
 $V = 1727.5$  (4) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.332$  Mg m<sup>-3</sup>  
Cu  $K\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta = 20.2\text{--}27.9^\circ$   
 $\mu = 1.62$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
Block, colourless  
 $0.6 \times 0.4 \times 0.3$  mm

## Data collection

Rigaku AFC-5S diffractometer  
 $\omega$  scans  
Absorption correction: analytical (de Meulenaer & Tompa, 1965)  
 $T_{\min} = 0.507, T_{\max} = 0.667$   
3507 measured reflections  
3283 independent reflections  
2118 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$   
 $\theta_{\text{max}} = 72.8^\circ$   
 $h = 0 \rightarrow 10$   
 $k = 0 \rightarrow 13$   
 $l = -21 \rightarrow 21$   
3 standard reflections  
every 150 reflections  
intensity decay: <2%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.130$   
 $S = 0.87$   
3283 reflections  
227 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0891P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.22$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.42$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

P1–O2	1.4717 (18)	P1–O4	1.6025 (16)
P1–O1	1.4770 (16)	O3–C31	1.392 (3)
P1–O3	1.6003 (15)	O4–C41	1.402 (3)
O2–P1–O1	120.33 (11)	O1–P1–O4	104.25 (9)
O2–P1–O3	105.07 (9)	O3–P1–O4	104.53 (9)
O1–P1–O3	111.02 (10)	C31–O3–P1	126.53 (13)
O2–P1–O4	110.67 (10)	C41–O4–P1	123.96 (14)

**Table 2**  
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O1^{ii}$	1.06 (3)	1.56 (3)	2.617 (3)	178 (3)
$N2-H2 \cdots O2$	0.90 (3)	1.75 (3)	2.633 (3)	170 (3)

Symmetry code: (ii)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ .

All methyl and phenyl H atoms were positioned geometrically and refined with a riding model; for methyl H atoms  $U_{iso}$  was constrained to be 1.5 times  $U_{eq}$  of the carrier atom and  $C-H = 0.96 \text{ \AA}$ ; for phenyl H atoms and H4 attached to the pyrazole ring  $U_{iso}$  was constrained to be 1.2 times  $U_{eq}$  of the carrier atom and  $C-H = 0.93 \text{ \AA}$ . The other H atoms, H1 and H2, were located in a difference map and refined isotropically.

Data collection: *MSC/AFM Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC/AFM Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

*PLATON* (Spek, 1998); software used to prepare material for publication: *PARST97* (Nardelli, 1996).

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